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PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Polymer Compositions

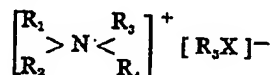
We, F. W. BERK & COMPANY LIMITED, a British Company of Berk House, 8 Baker Street, London, W.1, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is concerned with polymer compositions having anti-static properties and with the production of such compositions.

An undesirable feature of many synthetic polymers for certain applications is their ability to build up charges of static electricity. Attempts have been made to overcome this disadvantage by treating the surface of the polymer with certain compounds and it is also known to incorporate in the polymer organic compounds which impart anti-static properties to the polymer. Many of the anti-static compounds used hitherto have suffered the disadvantage of being thermo-labile and as a result polymers containing such compounds have been found to discolour badly upon heating the polymer, for example to the temperatures required for extrusion. The instability of such compounds manifests itself also in the small gas bubbles which form upon heating certain polymers, such as polystyrene, which contain anti-static compounds of the prior art.

We have now found that a certain class of organic quaternary ammonium salts are capable of imparting antistatic properties to synthetic polymers when incorporated in such polymers in small proportions and that the polymers containing said ammonium salts do not discolour or generate gas bubbles within the polymer upon heating the polymer to normal processing temperatures to the same extent as do synthetic polymers containing known anti-static compounds of the quaternary ammonium type, such as lauryl dimethyl ethyl ammonium ethosulphate and distearyl dimethyl ammonium chloride.

The organic quaternary ammonium salts for use in accordance with the invention have the formula:—



where R_1 is a straight chain alkyl group containing from 10 to 18 carbon atoms; R_2 and R_3 , which may be the same or different, are straight chain alkyl groups containing 1 to 6 carbon atoms; R_4 is a straight chain alkyl group containing from 1 to 6 or 10 to 18 carbon atoms; R_5 is a straight or branched chain alkyl or alkenyl group containing up to 18 carbon atoms, an aryl group such as phenyl or naphthyl, an aralkyl or alkaryl group the alkyl part of which contains up to 18 carbon atoms; and X is an anionic group, such as $-\text{COO}-$, $-\text{SO}_3-$, $-\text{PO}_3-$; X may be attached to the aromatic nucleus of R_5 when R_5 is an aralkyl or alkaryl group. These salts are in certain cases hereinafter referred to, for convenience, as the "anti-static agents".

Preferred anti-static agents are those in which R_1 is a straight chain alkyl group containing from 12 to 18 carbon atoms, advantageously from 16 to 18 carbon atoms; R_2 and R_3 are methyl or ethyl groups; R_4 is any one of the groups; methyl, ethyl, cetyl and stearyl; and R_5 is an aliphatic group containing from 10 to 18 carbon atoms or an aralkyl or alkaryl group the alkyl part of which contains from 10 to 18 carbon atoms. R_5X is advantageously an acid radical such as is contained in commercially available synthetic detergents or in soaps of vegetable or animal origin, X is preferably a carboxy or sulphonic acid group.

Specific suitable salts are, for example, distearyl dimethyl ammonium dodecyl benzene sulphonate, distearyl dimethyl ammonium palmitate, dicetyl dimethyl ammonium dodecyl

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benzene sulphonate, dicetyl dimethyl ammonium palmitate, distearyl dimethyl ammonium stearate, dicetyl dimethyl ammonium stearate, stearyl trimethyl ammonium dodecyl benzene sulphonate, cetyl trimethyl ammonium dodecyl benzene sulphonate, mixtures of said stearyl and cetyl trimethyl ammonium dodecyl benzene sulphonate prepared for instance from commercially available products containing both stearyl and cetyl compounds, lauryl dimethyl ethyl ammonium dodecyl benzene sulphonate, lauryl dimethyl ethyl ammonium palmitate, stearyl dimethyl ethyl ammonium stearate, and palmityl dimethyl butyl ammonium dodecyl benzene sulphonate.

The anti-static agents effectively confer anti-static properties upon a wide range of synthetic polymeric materials when incorporated in such materials, including, for example, polyvinyl compounds such as polyvinyl chloride, polyvinyl acetate and polystyrene, polyvinylidene compounds, polymers of allyl compounds, and polyolefines such as polyethylene and polypropylene. Copolymers, such as vinyl chloride-vinyl acetate copolymer, can also be effectively treated in accordance with the invention.

The proportion of the anti-static agent incorporated in the polymer will depend upon the nature of the polymer and the degree of anti-static properties which it is desired to impart to the polymer. Generally, less than 10% of the salt, by weight of the polymer, will be used. In many cases up to 5% of the salt, by weight of the polymer will be adequate, whereas with some polymers as little as 0.5% of the salt, by weight of the polymer, will impart sufficient anti-static properties to the polymer. With polystyrene, for instance, from 0.25% to 5%, but preferably 1% to 2%, of the salt, by weight of the polymer, may be used. With polyethylene, on the other hand, 2% to 3% of the salt, by weight of the polymer, is suitable, whereas for many applications as little as 0.1% in polyethylene will give a useful result.

The anti-static agents are, in general, waxy solids. Although they can be incorporated in synthetic polymers in this form there are

certain handling and processing difficulties associated with the use of the salts. As many of the polymers into which the salts are to be introduced are pulverulent solids, it is advantageous to transform the salts into pulverulent solids prior to incorporation in the polymer. We have found that this can be effected by combining the salt with an inorganic material which is substantially inert with respect to the polymer and the salt and has an oil-absorbing capacity. Useful inorganic materials which can be employed are those which are used as fillers in synthetic polymers, including those fillers which are also used as pigments. Mention may be made of the following inorganic materials which are suitable for combination with the anti-static agents:—silica, diatomaceous earth, calcium silicate, chalk, dolomite, barytes, barium sulphate, china clay, kaolin, and titanium dioxide.

The ratio of anti-static agent to inorganic material in such mixtures (which will hereinafter be referred to, for convenience, as the "anti-static additives") will in general be determined by the following factors:—the degree of fluidity desired of the mixture, the oil-absorptive power of the inorganic material (the greater the oil-absorptive power, the less inorganic material will be required to produce a given degree of dryness of solid, and vice-versa), and the maximum concentration of the anti-static agent which is compatible with the degree of fluidity desired of the anti-static additive.

In general, we find that the anti-static additive should contain at least one part of the salt for three parts of the inorganic material and no more than three parts of the salt per part of inorganic material, to give a solid product which can be readily incorporated in a pulverulent polymer composition.

Pulverulent anti-static additives have been prepared from distearyl dimethyl ammonium dodecyl benzene sulphonate, for example, with different proportions of certain inorganic materials, and the physical form of these anti-static additives is indicated below:—

Inorganic material	Parts by weight	Distearyl dimethyl ammonium dodecyl benzene sulphonate Parts by weight	Physical form of anti-static additive
"Dicalite" W.B.5.	2	1	particulate solid
"Aerosil"	1	2	particulate solid
"Aerosil"	1	1	free-flowing powder
Calcium silicate	1	2	particulate solid
Calcium silicate	1	3	particulate solid
"Gasil" 23	1	1	free-flowing powder
Titanium dioxide	3	1	lumpy solid

"Dicalite" = commercial diatomaceous earth; trade mark

"Aerosil" = commercial silica; trade mark

"Gasil" = commercial micronised silica gel; trade mark

5 The anti-static additive may be prepared, for example, by dissolving or suspending the salt in a suitable organic solvent (for instance, methyl ethyl ketone or acetone) and adding the inorganic material to the solution. After thorough mixing, the paste formed is dried to remove the volatiles leaving a particulate solid which does not usually require grinding.
10 Alternatively the salt can be melted and the inorganic material then added to it and thoroughly blended with it. This latter method does not require a drying step since there are no volatiles to be removed.

15 The anti-static agents or the anti-static additives may be incorporated in synthetic polymers in any suitable way. The compounding procedure to be used will vary according to the type and physical form of the polymer. It is convenient, however, to use a two roll mill (and press where necessary), the guide plates being set in at least one inch from each side of the rolls. The temperature to which the mill should be heated will vary according to the polymer; the following are 20 suitable temperatures for certain polymers:—
25

Polymer	Temperature		
	°C mill (steam exit temperature)	Corresponds to mill surface temperature	°C. press
Plasticised polyvinyl chloride (containing more than 10 parts of plasticiser per 100 of resin)	160	155	160
Polystyrene (GP and high impact)	160	155	150
Low density polyethylene	155	150	145
High density polyethylene	170	165	170
Vinyl chloride copolymer (14% acetate)	140	135	145
Rigid p.v.s. (all K values 55—65)	175	170	180
Polymethyl methacrylate	170	165	170
Acrylonitrile-butadiene-styrene terpolymer	160	155	160

For polymers in powder form, such as poly-
vinyl chloride powder, it is advisable to add
the anti-static agent as a 50% by weight solu-
tion or suspension in a suitable organic solvent
to the powder blend. Advantageously a con-
centrate or masterbatch of the anti-static agent
solution or suspension and a proportion of
the polymer is prepared by blending in a
Hobart mixer. The masterbatch may then be
introduced into the bulk of the polymer.
Alternatively, if a liquid additive, such as a
liquid plasticiser, is to be added to the poly-
mer, the liquid additive can be used as the
vehicle for the anti-static agent thus obviating
the use of an organic solvent.

With polymers in granular form, the anti-
static agent is conveniently added as a master-
batch to polymer banded on the front roll of
the mill. After addition of the anti-static agent
is complete, cross-blending is preferably
carried out at frequent intervals.

In some cases addition of the anti-static
agent is difficult since it causes over-lubrica-
tion and causes the batch to break up into
smaller pieces. Compounding can be achieved
in such cases by banding the polymer and
slowly adding the anti-static agent to the mill
without allowing the band to become disrupted,
and blending fully each aliquot of anti-static
agent added before making the next addition.
Use of an anti-static additive as described
above, rather than the anti-static agent *per se*,
may facilitate such compounding operations.

If desired the polymer composition con-
taining the anti-static agent may, after milling,
be granulated, extruded, re-granulated and
pressed into sheets.

The pressing of milled polymer is of par-
ticular significance in the resistivity testing of
polymers, which, after milling, do not possess
a surface which is sufficiently smooth for such
tests.

In order that the invention may be more
fully understood, the following examples are
given by way of illustration only, all parts and
percentages being by weight unless otherwise
stated.

In the examples, apart from Example 1,
the apparatus used for determining surface and
volume resistivities was Electronic Instruments
Limited Model 29 A, 20 million Megohmmeter,
with graphite electrodes. For surface resis-
tivity measurements the centre electrode was
attached to the high position, the outer elec-
trode to the low position and the square elec-
trode to the guard position on the megohmmeter.
For volume resistivity measurements, the
centre electrode was attached to the high posi-
tion, the square electrode to the low position
and the outer electrode to the guard position
on the megohmmeter. All samples submitted to
resistivity tests had a substantially uniform
thickness of about 0.05 inches.

Meter readings were after 1 minute from
the commencement of the test with the meter
set to 500 volts D.C. and the guard earthed.

The surface resistivity (S.R.) and volume resistivity (V.R.) were calculated from the following formulae:—

$$\text{S.R.} = \frac{2\pi R}{\log_e \frac{D}{d}} \text{ ohms}$$

$$= 2.06 \times 10^7 \times R \text{ ohms}$$

where D and d are electrode diameters and equal 10.15 cms. and 7.48 cms. respectively, and R is the meter reading.

$$\text{V.R.} = \frac{\pi \left(\frac{d}{2}\right)^2 \times R}{T}$$

$$= \frac{R \times 1.74 \times 10^7}{t} \text{ ohms cms.}$$

where T = thickness in cms. of sample
t = thickness in inches of sample
R = meter reading
d (electrode diameter) = 7.48 cms.

Samples for testing, measuring 6" x 6", were prepared as follows:—three concentric circles were drawn on the sample, the diameter of each corresponding to the diameters of the test electrodes. The areas of the centre circle and the outer ring left by the two outer circles were coated with a graphite dispersion and allowed to dry. The reverse side of each sample was also coated with the graphite dispersion to within $\frac{1}{4}$ inch of its edges and allowed to dry. When testing a sample, it was placed upon the square electrode, the outer electrode was placed on the outer graphite ring of the sample and the centre electrode on the central circle of graphite on the sample, taking due care to align the electrodes and graphite covered surfaces of the sample.

In Example 1, the equipment used for resistivity determinations was a Terraohmmeter, Type D3 made by Richard Jahre of Berlin. The electrodes and surrounding chamber are described in the Netherlands National

Standards HC NN—NEN 1514 of January 1957. (The electrodes are knife shaped and made of conducting rubber, 100 mms. long and 10 mms. apart).

Apart from resistivity determinations, the anti-static properties of the polymers were also evaluated by a dust pick-up test in certain cases. Long term dust pick-up was determined by punching a hole in a 2 $\frac{1}{4}$ by 6" sample and then hanging the sample vertically on a dust exposure rack for seven days. The sample was then compared with a blank, containing no anti-static agent, which had been similarly treated. The following rating for dust pick-up was used:—

no dust pick-up	1	
Light dust pick-up	2	
Heavy dust patterns—fern leaf branching	3	55

Short term dust pick-up was determined by rubbing the samples, which had been subjected to the long term dust pick-up test, with a fresh clean piece of cotton wool. Each sample was stroked twenty times in one direction only. The sample was then held $\frac{1}{4}$ " above a gently agitated tray of french chalk. The following rating for short term dust pick-up was used:—

No dust pick-up	1	65
Some dust pick-up	2	
Heavy dust pick-up	3	

Unless otherwise stated, in all the examples and comparative experiments, the samples were conditioned in a humidity chamber set at 23°C and between 50% and 53% relative humidity, for 24 hours prior to testing for resistivity or dust pick-up.

Determination of colour change on heating samples in air, referred to in the following examples, was effected in every case by placing a sample of the test material measuring 2" by 2" on an aluminium sheet measuring 6" by 6". The sample on the aluminium sheet was then placed in a forced draught oven and heated either at 180°C for 5 minutes or 250°C for 30 minutes. The colour of the sample was then noted.

EXAMPLE 1

Polyvinyl chloride compositions of the following composition were prepared:

		Parts
<u>Polymer</u>	Polyvinyl chloride resin sold under the trade mark "Corvic" D65/6 by I.C.I. Ltd.	100
<u>Plasticiser</u>	dioctyl phthalate	50
<u>Stabiliser</u>	tribasic lead sulphate sold under the trade name "Tribase" by F. W. Berk & Co. Ltd.	3
<u>Anti-static agent</u>	distearyl dimethyl ammonium dodecylbenzene sulphonate 0, $\frac{1}{4}$, $\frac{1}{2}$, 1, 2, and 5	

- 5 Polymer, plasticiser and stabiliser were pre-mixed in a glass beaker by hand with a spatula. The premix was added to a two roll mill so as to form a band of fluxed material in 1—2 minutes. The roll temperatures of the mill were: front 135°C, back 125°C. The mill was on friction ratio, i.e. the back roll turned 1.15 revolutions to each revolution of the front.
- 10 The weighed amount of anti-static agent was added gradually so that the mixture did not fall from the rolls. The anti-static agent has a lubricating action, and if added all at once to the mixture causes the mixture to fall
- 15 from the rolls. In the case of the lower amounts of anti-static agent, addition was effected over

6 minutes and in the case of the higher amounts, it was effected over 14 minutes. The mixture was cross blended continuously during the milling operation.

After the final addition of the anti-static agent, a further minute of milling was carried out to ensure complete blending.

The hide (0.050 inches thick) was wrapped immediately in regenerated cellulose film and allowed to cool. Two 6" x 8" rectangles were cut from the cooled hide and also wrapped in regenerated cellulose film.

The surface resistivity of the sample was determined at 26°C with the following results:

Meter Readings in Megohms

Antistatic Agent No. of Pans	Sample	Side 1	Side 2
0	1	$5.5 \times 10^5, 4.3 \times 10^5$	$4.0 \times 10^5, 2.0 \times 10^5, 3.0 \times 10^5$
	2	$5 \times 10^5, 3 \times 10^5, 3 \times 10^5$	$2.7 \times 10^5, 8 \times 10^4$
$\frac{1}{4}$	1	$1.3 \times 10^4, 2.2 \times 10^4, 1.12 \times 10^5$	$1.3 \times 10^4, 1.6 \times 10^4$
	2	$1.1 \times 10^3, 1.6 \times 10^3$	$1.2 \times 10^3, 1.2 \times 10^3$
$\frac{1}{2}$	1	$4.1 \times 10^3, 4.6 \times 10^3$	$4.0 \times 10^3, 4.8 \times 10^3$
	2	$4.5 \times 10^3, 5.3 \times 10^3$	$3.9 \times 10^3, 6.0 \times 10^3, 3.8 \times 10^3$
1	1	$5.0 \times 10^3, 1.2 \times 10^3$	$5.2 \times 10^3, 6.8 \times 10^3$
	2	$6.2 \times 10^3, 5.5 \times 10^3$	$5.5 \times 10^3, 7.8 \times 10^3, 5.3 \times 10^3$
2	1	$3.6 \times 10^3, 8.0 \times 10^3, 3.9 \times 10^3$	$3.0 \times 10^3, 8.0 \times 10^3, 4.0 \times 10^3$
	2	$3.8 \times 10^3, 4.6 \times 10^3$	$3.5 \times 10^3, 5.0 \times 10^3, 3.5 \times 10^3$
5	1	$1.9 \times 10^3, 2.5 \times 10^3, 2.5 \times 10^3$	$2.4 \times 10^3, 2.8 \times 10^3$
	2	$1.9 \times 10^3, 2.5 \times 10^3$	$2.2 \times 10^3, 3.0 \times 10^3, 2.2 \times 10^3$

EXAMPLE 2

A flexible polyvinyl composition of the following formulation was prepared:—

		Parts
<u>Polymer</u>	Polyvinyl chloride resin sold under the trade mark "Breon" 112 by British Geon Ltd.	100
<u>Plasticiser</u>	dioctyl phthalate	30
<u>Stabiliser</u>	organo cadmium-barium compound sold under the trade mark "Flomax" 25 by F. W. Berk & Co. Ltd.	3
<u>Anti-static Agent</u>	distearyl dimethyl ammonium dodecyl benzene sulphonate	0, $\frac{1}{4}$, $\frac{1}{2}$, $\frac{3}{4}$, 1, $1\frac{1}{2}$, $1\frac{3}{4}$

5 The polymer composition was compounded in a manner similar to that described in Example 1, and tested in the way described above for resistivity and dust pick-up with the following results:—

Parts of anti-static agent	SR after 1 week ohms	VR after 1 week ohms. cms.	VR after 15 weeks ohms. cms.	Dust attraction	
				short term	long term
0	1.4×10^{14}	1.7×10^{14}	$>4 \times 10^{14}$	2	trace
$\frac{1}{4}$	1.43×10^{13}	1.24×10^{13}	1.10×10^{11}	1	1
$\frac{1}{2}$	2.24×10^{12}	2.20×10^{11}	2.50×10^{11}	1	1
$\frac{3}{4}$	2.46×10^{12}	2.52×10^{11}	2.46×10^{11}	1	1
1	2.66×10^{12}	2.35×10^{11}	2.40×10^{11}	1	1
$1\frac{1}{4}$	1.76×10^{12}	2.38×10^{11}	2.20×10^{11}	1	1
$1\frac{3}{4}$	1.57×10^{12}	1.56×10^{11}	1.74×10^{11}	1	1

10

EXAMPLE 3

A rigid vinyl chloride-vinyl acetate copolymer composition of the following formulation was prepared (the copolymer contained 14% of the acetate):—

		Parts
<u>Polymer</u>	V.C./V.A. copolymer	100
<u>Stabiliser</u>	dibutyl tin maleate	10
<u>Anti-static Agent</u>	distearyl dimethyl ammonium dodecyl benzene sulphonate	5

The copolymer was milled as described testing for surface resistivity as described in Example 1 and then pressed into sheets for above: the following results were obtained:—

Parts of Anti-static Agent	S.R. ohms	Short term dust pick-up
0	$>10^{14}$	3
5	2.4×10^{13}	1

EXAMPLE 4

A rigid vinyl chloride-vinyl acetate copolymer composition of the following formula- 14% of the acetate):— 10

		Parts
Polymer	V.C./V.A. copolymer	100
Stabiliser	tribasic lead sulphate sold under the trade name "Tribase" by F. W. Berk & Co. Ltd.	10
Anti-static Agent	distearyl dimethyl ammonium dodecyl benzene sulphonate	5

The copolymer was compounded with the anti-static agent as described in Example 3 and tested for surface resistivity and dust pick-up as in Example 3, with the following results:— 15

Parts of Anti-static Agent	S.R. ohms	Short term dust pick-up
0	$<10^{14}$	3
5	3.6×10^{13}	3
5	1.9×10^{13}	3

EXAMPLE 5

A toughened polystyrene composition was prepared in accordance with the following formulation:— 20

		Parts
Polymer	Polystyrene sold under the trade mark "Carinex" natural by Shell Chemical Ltd.	100
Anti-static Agent	distearyl dimethyl ammonium dodecyl benzene sulphonate	1
Inorganic material	diatomaceous earth sold under the trade name "Dicalite" WB5 by F. W. Berk & Co. Ltd.	2

- The anti-static agent and inorganic material were thoroughly mixed together and a masterbatch was prepared from the mixture and "Carinex" natural. The masterbatch was then added to the bulk of the "Carinex" natural on the mill. The composition was milled at 155°C (mill surface temperature) and pressed (at 150°C) into sheets which were then processed for heat stability testing as described above.
- 10 Heat stability tests at 250°C for 30 minutes
- 15 were carried out on the above samples, with a blank (which differed from the test samples in that it did not contain anti-static agent or diatomaceous earth) and a sample containing 1 part of lauryl dimethyl ethyl ammonium etho-sulphate per 100 parts of resin, for comparative purposes. All samples were examined for gas bubble formation after the heating operation.

Anti-static agent	colour of polymer after heating		Gas formation
	exposed surface	underside	
nil	light brown	off-white	none
distearyl dimethyl ammonium dodecyl benzene sulphonate	medium brown	off-white	none
lauryl dimethyl ethyl ammonium etho-sulphate	dark brown	pale yellow	severe

EXAMPLES 6 TO 11

Example 5 was repeated but "Dicalite" was replaced by different proportions of various other inorganic materials. The resistivity and dust pick-up results are tabulated below:—

Example No.	Inorganic Material	Parts of inorganic material	Parts of Antistatic Agent	S.R. (ohms)	V.R. (ohm. cms.)	Dust Pick-up	
						Long term	Short term
6	"Aerosil"	$\frac{1}{2}$	1	3.76×10^{13}	2.6×10^{14}	2	2
7	"Aerosil"	1	1		3.1×10^{14}	1	2
8	Calcium silicate	$\frac{1}{2}$	1		2.4×10^{14}	1	2
9	Calcium silicate	$\frac{1}{3}$	1		2.5×10^{14}	1	2
10	"Gasil" 23	1	1			1	2
11	Titanium dioxide	3	1	1.53×10^{13}	—	1	2

Heat stability tests were carried out with 5 control containing the same proportion of the compositions of each of the above examples. When compared with a blank and a lauryl dimethyl ethyl ammonium ethosulphate as that of the antistatic agent in each example, results similar to those described in Example 5 were obtained.

EXAMPLE 12

A polystyrene composition of the following formulation was prepared:—

		Parts
Polymer	"Carinex" natural	100
Anti-static Agent	distearyl dimethyl ammonium dodecyl benzene sulphonate	0.25; 0.50; 0.75; 1.00; 1.25; 1.50; 3.00; 6.25; 10.0
Inorganic Material	titanium dioxide	3 parts per part of anti-static agent

- 5 A 50% solution of the anti-static agent in methyl ethyl ketone was added slowly to the titanium dioxide and the whole mixed into a smooth paste. The paste was spread out on a tray and heated in an oven at 100°C for 45 minutes. After removal of the tray from the oven, the mass of anti-static additive was broken up and re-heated for a further 15 minutes at 100°C to ensure removal of volatiles.
- 10 The anti-static additive thus prepared was added slowly to the polystyrene in the mill as described in the foregoing examples. The resultant product was pressed into sheets and prepared for resistivity and dust pick-up tests as described above.
- 15

Parts of Anti-static Agent	S.R. (ohms)	Dust pick-up	
		long term	short term
0	4×10^{14}	3	3
0.25	a) 1.0×10^{14} b) 1.5×10^{14}	2	3
0.50	a) 7.1×10^{13} b) 5.0×10^{13}	2	3
0.75	a) 2.0×10^{13} b) 4.2×10^{13}	2	3
1.00	a) 4.1×10^{13} b) 3.1×10^{13}	1	2
1.25	a) 1.5×10^{13} b) 2.5×10^{13}	1	2
1.50	a) 2.8×10^{13} b) 2.2×10^{13}	1	1
3.00	a) 2.2×10^{13} b) 1.3×10^{13}	1	1
6.25	a) 7.8×10^{12} b) 5.6×10^{12}	1	1
10.0	a) 2.0×10^{12} b) 2.0×10^{12}	1	1

EXAMPLE 13

Example 12 was repeated using a formulation containing 1 part of the anti-static agent and 3 parts of titanium dioxide per 100 parts of the polystyrene sold under the trade mark "Distrene" Q-9015 by Distrene Ltd. The surface resistivity of this formulation was found to be 1.18×10^{13} ohms.

EXAMPLE 14

Example 13 was repeated but "Distrene" Q-9015 was replaced by the polystyrene sold under the trade mark "Bextrene" BC15 by B.X. Plastics Ltd. The surface resistivity of this formulation was found to be 6.0×10^{13} ohms.

EXAMPLE 15

A high density polyethylene composition of the following formulation was prepared:—

Parts		
Polymer	High density polyethylene sold under the trade mark "Rigidex" (Natural 9) by British Resin Products Ltd.	100
Anti-static Agent	distearyl dimethyl ammonium dodecyl benzene sulphonate	1
Inorganic material	titanium dioxide	3

20 An anti-static additive was prepared from the anti-static agent and titanium dioxide in a manner similar to that described in Example 12.

25 The additive thus prepared was compounded with "Rigidex" (Natural 9) in a manner similar to that used for compounding the additive with

polystyrene in Example 12. The mill surface temperature was, however, 165°C and the temperature of the press 170°C .

Samples of the resultant product were prepared for resistivity and dust pick-up tests as already described and the following results were obtained:—

Parts of anti-static agent	S.R. (ohms)
0	$> 10^{14}$
1	1.7×10^{13}

35

EXAMPLE 16

A high density polyethylene composition of the following formulation was prepared:—

Parts		
Polymer	"Rigidex" Natural 9	100
Anti-static Agent	distearyl dimethyl ammonium dodecyl benzene sulphonate	0.05; 0.10; 0.25; 0.50; 0.75; 1.00; 2.00; 3.00; 5.00
Inorganic material	titanium dioxide	3 parts per part of anti-static agent

40 The process described in Example 15 was repeated for each concentration of anti-static agent specified in the above formulation.

Samples were prepared for testing in the manner already described and the results obtained were as follows:—

Parts of anti-static agent	S.R. (ohms)	Dust pick-up		Colour of underside of polymer after heating	
		long term	short term	5 mins. at 180° C.	30 mins. at 250° C.
0	$>4 \times 10^{14}$	2	3	white	off-white
0.05	$>4 \times 10^{14}$	2	3		
0.10	$>4 \times 10^{14}$	2	3		
0.25	2.0×10^{14}	2	3		
0.50	1.6×10^{13}	2	3		
0.75	7.2×10^{12}	1	3		
1.00	4.2×10^{12}	1	2	white	cream
2.00	2.0×10^{12}	1	1		
3.00	9.3×10^{11}	1	1		
5.00	6.3×10^{11}	1	1		

Comparative Experiment 1

5 A high density polyethylene composition of the above formulation was prepared, but 1 part of lauryl dimethyl ethyl ammonium etho-sulphate was substituted for the distearyl dimethyl ammonium dodecyl benzene sul-phionate.

The polyethylene formulation was com-pounded in a manner identical to that described in Example 16 and the heat stability deter-mined as in Example 16 with the following results:—

Colour of underside of polymer after heating	
5 mins. at 180° C.	30 mins. at 250° C.
off-white	pale brown

15

EXAMPLE 17

A low density polyethylene composition of the following formulation was prepared:—

		Parts
Polymer	Low density polyethylene sold under the trade mark "Alkathene" XDG33 by I.C.I. Ltd.	100
Anti-static Agent	distearyl dimethyl ammonium dodecyl benzene sulphonate	0.25; 0.50; 0.75; 1.00; 1.25; 1.50; 2.00; 3.00; 5.00;
Inorganic material	titanium dioxide	3 parts per part of anti-static agent

The compounding process used was that described in Example 15 except that the mill surface temperature was 150°C and the press temperature 145°C. Samples of the formulated

low density polyethylene were prepared and tested for surface resistivity and dust pick-up in the manner already described, with the following results:—

5

Parts of Anti-static agent	S.R. (ohms)	Dust pick-up	
		long term	short term
0	$>4 \times 10^{14}$	3	3
0.25	4.1×10^{14}	3	3
0.50	3.0×10^{13}	2	3
0.75	a) 1.5×10^{13} b) 2.2×10^{13}	1	3
1.00	a) 9.4×10^{12} b) 10.1×10^{12}	1	1
1.25	a) 4.1×10^{12} b) 7.3×10^{12}	1	1
1.50	a) 4.9×10^{12} b) 7.6×10^{12}	1	1
2.0	a) 4.7×10^{12} b) 8.4×10^{12}	1	1
3.0	a) 6.8×10^{12} b) 4.3×10^{12}	1	1
5.0	a) 4.5×10^{12} b) 5.1×10^{12}	1	1

10

EXAMPLES 18 TO 21

A toughened polystyrene composition of the following formulation was prepared:—

		Parts
Polymer	"Carinex" natural	100
Anti-static Agent	as specified hereinafter	1

In each case the anti-static agent was mixed with a part of the whole quantity of the "Carinex" natural and this mixture or master-batch was added to the mill (surface tempera-

15

ture of 155°C). The composition was then processed substantially as described in Example 5. Surface resistivity and dust pick-up tests gave the following results:—

20

Example No.	Anti-static agent	S.R. (ohms)	Dust pick-up	
			long term	short term
18	distearyl dimethyl ammonium palmitate	4.7×10^{13}	1	3
19	distearyl dimethyl ammonium stearate	3.0×10^{14}	1	3
20	distearyl dimethyl ammonium cetostearyl sulphate	2.0×10^{14}	1	2
21	distearyl dimethyl ammonium p-toluene sulphonate	1.2×10^{13}	1	1
—	none (as blank)	$>4 \times 10^{14}$	3	3

EXAMPLE 22

A high density polyethylene composition was compounded from 1 part of distearyl dimethyl ammonium p-toluene sulphonate per 100 parts of "Rigidex" Natural 9, in the manner described in Example 15, except that the step of preparing an anti-static additive was omitted. The surface resistivity of the compounded "Rigidex" Natural 9 was determined

and compared with that of an identically treated polymer which did not contain an anti-static agent. The surface resistivity of the blank was found to be greater than 10^{14} ohms whereas that of the sample containing the anti-static agent was 1.9×10^{11} ohms.

EXAMPLE 23

A high density polyethylene composition of the following formulation was prepared:—

Parts		
Polymer	"Rigidex" Natural 9	100
Anti-static Agent	distearyl dimethyl ammonium palmitate	1
Inorganic material	"Gasil" 23	1

A paste was prepared by adding a 50% dispersion of the anti-static agent in an organic solvent to the "Gasil". The paste was dried thoroughly in an oven at 100°C and fragmented.

The anti-static additive thus prepared was masterbatched with a proportion of the "Rigidex" Natural 9 and the masterbatch milled into the bulk of the polyethylene as already described in the foregoing examples.

Samples of the compounded polymer were prepared and tested for dust pick-up. The short term dust pick-up was found to be 2, whereas a sample which, apart from not containing an anti-static agent, had been subjected to identical processing conditions was found to have a short term dust pick-up of 3.

EXAMPLE 24

A toughened polystyrene composition of the following composition was prepared:—

Parts		
Polymer	"Carinex" Natural	100
Anti-static Agent	Cetostearyl* trimethyl ammonium dodecyl benzene sulphonate	1

* Cetostearyl is used herein to denote the C_{18}/C_{17} cut obtained from natural oils, for example, and is a mixture of cetyl and stearyl residues.

The cetostearyl trimethyl ammonium dodecyl benzene sulphonate was premixed with a small proportion of the polystyrene and then added to a two roll mill so as to form a band of fluxed material in a few minutes.

The fluxed material was then gradually added to a two roll mill in which the bulk of the polystyrene was milled, the mixture being continuously cross-blended. The milling operation took 5 minutes and the roll tempera-

ture of the front of the mill was 155°C.

The resultant product was then pressed for 5 minutes at 155°C to provide a smooth hide of about 0.05 inch thickness from which samples were made for resistivity and heat stability tests.

The surface resistivity was found to be 1.0×10^{11} ohms.

The colour of the samples was found to be as follows:—

Initial colour (i.e. after pressing but prior to oven heating)	Colour after 5 mins. at 180° C.	Colour after 30 mins. at 250° C.	
		Exposed surface	Underside
off-white	off-white	off-white	brown

Comparative Experiment 2

Two samples of "Carinex" Natural were processed as described above, the only difference being that one of the two samples did not contain an anti-static agent, whereas the other contained 1 part of "Dacol" (a commercially available dimethyl distearyl am-

monium chloride) per 100 parts of the polystyrene.

The surface resistivity and the colour changes produced on heating were determined for these samples in a manner identical with that described in the Example, and the following results were obtained:

	Surface Resistivity (ohms)	Initial colour	Colour after 5 mins. at 180° C.	Colour after 30 mins. at 250° C.	
				exposed surface	underside
Blank	$>4 \times 10^{14}$ *	off-white	off-white	light brown	pale yellow
"Dacol"- containing sample	5.1×10^{11}	buff	brown	dark brown	light brown

(* maximum reading on Megohmmeter = 4×10^{14} ohms)

These results show that the anti-static properties of the polystyrene containing cetostearyl trimethyl ammonium dodecyl benzene sulphonate were greater than those of the polystyrene containing the same proportion of the commercially available "Dacol". Further-

more, the colour degradation on heating was less with the former composition than for the "Dacol"-containing composition.

EXAMPLE 25

A high density polyethylene composition of the following formulation was prepared:—

Parts		
Polymer	"Rigidex" Natural 9	100
Anti-static Agent	Cetostearyl trimethyl ammonium dodecyl benzene sulphonate	1

The composition was compounded in a manner similar to that described in Example 24, except that the milling and pressing temperatures were both 170°C.

Surface resistivity and colour degradation on heating were determined as described in Example 24 with the following results:—

Surface Resistivity (ohms)	Initial colour	Colour after 5 mins. at 180°C.	Colour after 30 mins. at 250°C.	
			Exposed Surface	Underside
2.4×10^{10}	white	white	brown	pale yellow

10 *Comparative Experiment 3*
Experiments similar to those described under Comparative Experiment 2 above were carried

out using "Rigidex" Natural 9 in place of "Carinex" Natural. The results obtained are given below:—

	Surface Resistivity (ohms)	Initial Colour	Colour after 5 mins. at 180°C.	Colour after 30 mins. at 250°C.	
				Exposed Surface	Underside
Blank	$>10^{14}$	white	white	pale brown	off-white
"Dacol"-containing sample	6.1×10^{11}	off-white	off-white	brown	yellow

EXAMPLE 26

A flexible polyvinyl chloride resin composition of the following formulation was prepared:—

		Parts
Polymer	"Geon" 112 (trade mark)	100
Plasticiser	Diocetyl phthalate	30
Stabiliser	"Flomax" 25	5
Anti-static Agent	Cetostearyl trimethyl ammonium dodecyl benzene sulphonate	1

20 The anti-static agent was blended with the plasticiser and stabiliser and added to the resin as it passed through the two roll mill (155°C).
25 Milling and cross blending were carried out for 5 minutes. The surface of the hide produced was sufficiently smooth for surface and volume

resistivity determinations and the sample was therefore not pressed.

Samples were prepared for resistivity tests and examined for colour. The following results were obtained:—

Volume Resistivity (ohm. cms.)	Initial Colour
10.2×10^{10}	some yellowing

Comparative Experiment 4

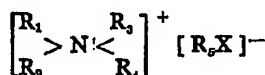
Two samples of the polyvinyl chloride resin "Geon" were formulated as described in the Example with the difference that one sample did not contain an anti-static agent and the

other contained 1 part of "Dacol" instead of cetostearyl trimethyl ammonium dodecyl benzene sulphonate. Volume resistivity and colour determinations were made as in the Example with the following results:—

	Volume resistivity (ohm. cms.)	Initial Colour
Blank	6.8×10^{13}	trace of yellowing
"Dacol"— containing sample	6.5×10^{10}	orange

WHAT WE CLAIM IS:—

1. A synthetic polymer composition having anti-static properties which comprises a synthetic organic polymer having incorporated therein up to 10%, by weight of the organic polymer, of a quaternary ammonium compound of the formula:



wherein R_1 and R_2 , which may be the same or different, are straight chain alkyl groups containing from 10 to 18 carbon atoms, R_3 and R_4 , which may be the same or different, are straight chain alkyl groups containing from 1 to 6 carbon atoms, R_5 is a straight or branched chain alkyl or alkenyl group containing up to 18 carbon atoms, an aryl group, or an aralkyl or alkaryl group, the alkyl residue of which contains up to 18 carbon atoms, and X is an anionic group.

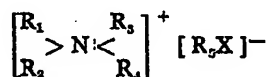
2. A composition according to claim 1, in which R_1 and R_2 contain from 16 to 18 carbon atoms, R_3 and R_4 are methyl groups, R_5 is an aliphatic group containing from 10 to 18 carbon atoms or an alkaryl group, the alkyl residue of which contains from 10 to 18 carbon atoms, and X is $-\text{COO}^-$, $-\text{SO}_3^-$ or $-\text{PO}_3^{--}$.

3. A composition according to claim 1 or 2, in which the quaternary ammonium salt is distearyl dimethyl ammonium dodecyl benzene sulphonate, distearyl dimethyl ammonium palmitate, dicetyl dimethyl ammonium dodecyl benzene sulphonate, dicetyl dimethyl ammonium palmitate, distearyl dimethyl ammonium stearate or dicetyl dimethyl ammonium stearate.

4. A composition according to any of claims 1 to 3, which comprises from 0.25 to 5% of the quaternary ammonium salt based on the weight of the organic polymer.

5. A synthetic polymer composition having anti-static properties which comprises a synthetic organic polymer having incorporated

therein up to 10%, by weight of the organic polymer, of a quaternary ammonium compound of the formula:



where R_1 is a straight chain alkyl group containing from 10 to 18 carbon atoms, R_2 , R_3 and R_4 which may be the same or different, are straight chain alkyl groups containing from 1 to 6 carbon atoms, R_5 is a straight or branched chain alkyl or alkenyl group containing up to 18 carbon atoms, an aryl group, or an aralkyl or alkaryl group, the alkyl residue of which contains up to 18 carbon atoms, and X is an anionic group.

6. A composition according to claim 5, in which R_1 is a straight chain alkyl group containing from 16 to 18 carbon atoms, R_3 , R_4 and R_5 are methyl or ethyl groups, R_6 is an alkyl group containing from 10 to 18 carbon atoms or an aralkyl or alkaryl group, the alkyl residue of which contains from 10 to 18 carbon atoms, and X is $-\text{COO}^-$, $-\text{SO}_3^-$ or $-\text{PO}_3^{--}$.

7. A composition according to claim 4 or 5, in which the quaternary ammonium compound is stearyl trimethyl ammonium dodecyl benzene sulphonate, cetyl trimethyl ammonium dodecyl benzene sulphonate, a mixture of stearyl trimethyl ammonium dodecyl benzene sulphonate and cetyl trimethyl ammonium dodecyl benzene sulphonate, lauryl dimethyl ethyl ammonium dodecyl benzene sulphonate, lauryl dimethyl ethyl ammonium palmitate, stearyl dimethyl ethyl ammonium stearate, or palmityl dimethyl butyl ammonium dodecyl benzene sulphonate.

8. A composition according to any of claims 5 to 7, which comprises from 0.25 to 5% of the quaternary ammonium salt based on the weight of the organic polymer.

9. A composition according to any of claims 1 to 8, which additionally comprises from 1 to 9 parts by weight of a finely divided in-

organic material having an oil-absorptive capacity for each 3 parts by weight of the quaternary ammonium compound.

- 5 10. A composition according to claim 9, in which the inorganic material is silica, chalk, dolomite, diatomaceous earth, calcium silicate, barytes, barium sulphate, china clay, kaolin or titanium dioxide.
- 10 11. A particulate composition capable of imparting anti-static properties to a synthetic organic polymer when incorporated therein, which consists of an intimate mixture of from one to nine parts by weight of a pulverulent inorganic material having an oil-absorptive capacity and three parts by weight of a quaternary ammonium compound as defined in any of
- 15 claims 1, 2, 3, 5, 6 or 7.
- 20 12. A particulate composition according to claim 11, in which the inorganic material is silica, chalk, dolomite, diatomaceous earth, calcium silicate, barytes, barium sulphate, china clay, kaolin or titanium dioxide.
- 25 13. A process for the preparation of a synthetic polymer composition having anti-static properties, which comprises introducing into a synthetic organic polymer up to 10%, based on the weight of the organic polymer, of a quaternary ammonium salt as defined in any of claims 1, 2, 3, 5, 6 or 7.
- 30 14. A process according to claim 13, in which the quaternary ammonium salt is in the molten state when incorporated into the organic polymer.
- 35 15. A process according to claim 13, in which the quaternary ammonium salt is dispersed in a liquid additive for the polymer and the resulting dispersion is incorporated in the polymer.
- 40 16. A process according to claim 15, in which the liquid additive is a stabiliser, plasticiser or anti-oxidant for the polymer.
17. A process according to claim 13, in which the quaternary ammonium salt is intimately mixed with a pulverulent inorganic

material having an oil-absorptive capacity in the ratio of one to nine parts by weight of the inorganic material for every three parts by weight of the quaternary ammonium salt, and the intimate mixture is incorporated in the polymer.

18. A process according to claim 17, in which the quaternary ammonium salt is melted and mixed, in the molten state, with the inorganic material.

19. A process according to claim 17, in which the quaternary ammonium salt is dissolved or dispersed in an organic solvent, the solution or dispersion is intimately mixed with the inorganic material, and the mixture is then dried and, if necessary, ground to yield a particulate solid which is incorporated in the polymer.

20. A process according to any of claims 17 to 19, in which the inorganic material is silica, chalk, dolomite, diatomaceous earth, calcium silicate, barytes, barium sulphate, china clay, kaolin or titanium dioxide.

21. A process according to any of claims 13 to 19, in which from 0.25 to 5% of the quaternary ammonium salt, based on the weight of the polymer, is incorporated in the latter.

22. A synthetic polymer composition according to claim 1 substantially as herein described in Example 1.

23. A synthetic polymer composition according to claim 5 substantially as herein described in either of Examples 24 or 25.

24. A synthetic polymer composition according to claim 1 substantially as herein described in any of Examples 2—23.

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Int. Cl.:—C 08 f

COMPLETE SPECIFICATION

Polymer Compositions

ERRATA

SPECIFICATION No. 1,014,539
Amendment No. 1

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Page 4, in the table, under the heading "Polymer." for "Rigid p.v.s." read "Rigid p.v.c."

Page 9, Example 4, second table, under the heading "S.R. ohms." for "<10¹⁴" read ">10¹⁴"

Page 12, Example 12, second table, first result given in the column headed "S.R. (ohms)" for "4×10¹⁴" read ">4×10¹⁴"

Page 19, line 61, for "R₁" read "R₂."

THE PATENT OFFICE
25th February 1966

CORRECTION OF CLERICAL ERROR

SPECIFICATION NO. 1,014,539

AMENDMENT NO. 2

The following correction is in accordance with the Decision of the Senior Examiner, acting for the Comptroller-General dated the eleventh day of July,

Page 20, line 78, for "either of Examples 24 or 25." insert "any of Examples 24, 25 or 26."

THE PATENT OFFICE,
22nd September, 1966

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